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Formation of Complexes from Azobenzenes and Cyclopentadienyl Cobalt Derivatives[*1]

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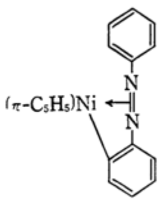
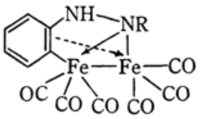
New complexes (III) have been found to be formed in the reaction between aromatic azo compounds and cyclopentadienyl cobalt derivatives. The same complexes have also been obtained from the reaction of *o*-quinonediimine or *o*-phenylenediamine derivatives with cyclopentadienyl cobalt dicarbonyl. These complexes reacted with carbon monoxide to yield benzimidazolone derivatives, and with hydrogen to give *o*-phenylenediamine derivatives. The structure of the complexes has been formulated on the basis of the infrared spectra, the proton magnetic resonance, and chemical evidence.

The formation of the complex (I) from the reaction of azobenzene with dicyclopentadienyl nickel has been reported by Kleiman and Dubeck.[1] Complexes with a similar structure have been isolated from the reaction between azobenzene or its derivatives and potassium tetrachloroplatinate or palladium dichloride.[2]



(I)



(II)

Azobenzene complexes of iron (II) have recently been reported on by Bagga, Pauson, Preston, and Reed.[3]

We wish to present a report on the formation of new complexes from azobenzenes and cyclopentadienyl cobalt derivatives.

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1) J. P. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963).

2) A. C. Cope and R. W. Siekman, *ibid.*, **87**, 3272 (1965).

3) M. M. Bagga, P. L. Pauson, F. J. Preston and R. I. Reed, *Chem. Commun.*, **1965**, 543.

Experimental

The infrared spectra were obtained in KBr pellets on a Jasco Model DC-402G spectrophotometer. The NMR spectra were recorded by a Varian Model A-60 instrument, using tetramethylsilane as an internal standard in carbon disulfide. All the melting points are uncorrected; they were measured by a micro-melting point apparatus, Yanagimoto Model MP-S2.

Reaction between Azobenzene and Cyclopentadienyl Cobalt Dicarbonyl. A mixture of 5 g of cyclopentadienyl cobalt dicarbonyl and 5 g of azobenzene was heated at 160°C for 3.5 hr under a nitrogen atmosphere. During this period, the reaction proceeded and gas was evolved. The reaction mixture was extracted with a small portion of benzene and chromatographed on alumina using a mixture of *n*-hexane and benzene (1 : 1) as a developer. The recrystallization from *n*-hexane gave the complex IIIa as red-purple crystals; mp 162—163°C. The yield was 39%.

Found: C, 66.70; H, 4.95; N, 9.01%; mol wt, 298 (cryoscopic in benzene). Calcd for $C_{17}H_{15}N_2Co$: C, 66.67; H, 4.94; N, 9.15%; mol wt, 306.

IR: 3310(w), 3040(vw), 1586(m), 1574(m), 1482(s), 1462(m), 1444(m), 1400(w), 1370(s), 1362(s), 1335(s), 1276(m), 1215(s), 1175(w), 1146(m), 1116(sh), 1108(m), 1065(w), 1050(w), 1020(w), 1000(m), 921(w), 910(vw), 895(vw), 865(w), 833(m), 820(s), 752(vs), 699(m) cm^{-1}.

Reaction between Azobenzene and Dicyclopentadienyl Cobalt. A mixture of 5 g of dicyclopentadienyl cobalt and 20 g of azobenzene was heated at 135°C for 3.5 hr, after which the reaction mixture was treated as has been described above. The complex IIIa was obtained in a 2.4% yield.

Formation of the Complex from 4, 4′-Dimethylazobenzene and Cyclopentadienyl Cobalt Dicarbonyl. A solution of 3 g of 4, 4′-dimethylazobenzene and 2.5 g of cyclopentadienyl cobalt dicarbonyl in 30 m*l* of xylene was refluxed for 4 hr, and then the reaction mixture was chromatographed and recrystallized to yield the red-purple crystals of IIIb in a 13% yield; mp 172—173°C.

Found: C, 68.52; H, 5.81; N, 8.27%. Calcd for $C_{19}H_{19}N_2Co$: C, 68 26; H, 5.73; N, 8.38%.

IR: 3320(m), 3020(vw), 2910(vw), 2850(vw), 1580(w), 1499(m), 1407(w), 1380(w), 1358(s), 1338(m), 1315(w), 1263(m), 1221(m), 1180(sh), 1174(m), 1148(w), 1120(w), 1118(m), 1045(w), 1100(m), 894(w), 865(w), 847(vw), 835(w), 803(s), 749(m), 710(m) cm^{-1}.

Reaction of (π-C_5H_5)Co($C_{12}H_{10}N_2$) and Carbon Monoxide. A solution of the complex IIIa (1 g) in benzene (10 m*l*) was placed in an autoclave with a capacity of 100 m*l*, and then carbon monoxide was charged in up to 100 kg/cm². The autoclave was heated at 200°C for 6 hr under constant shaking. After cooling, the benzene was removed from the reaction mixture. The residue was washed with *n*-hexane, treated with a 5% aqueous solution of sodium hydroxide, and filtered. When the alkaline solution was acidified by hydrochloric acid, a white crystalline substance separated. The crystalline substance, after filtration, was recrystallized from benzene, yielding a 60% yield of *N*-phenylbenzimidazolone, mp 207—208°C, which was identified by a mixed-melting-point test with an authentic sample[4] and by a study of its infrared spectrum. After the *N*-phenylbenzimidazolone had been removed, the *n*-hexane solution was chromatographed on alumina to give 0.2 g of cyclopentadienyl cobalt dicarbonyl.

Reaction of (π-C_5H_5)Co($C_{12}H_{10}N_2$) and Hydrogen. A solution of the complex IIIa (3 g) in benzene (50 m*l*) was placed in an autoclave with a capacity of 100 m*l* and then reacted with 100 kg/cm² of hydrogen at 200°C for 6 hr. After the reaction solution had been let stand to room temperature, the benzene was removed from the reaction mixture. The residue was treated with *n*-hexane to yield colorless needle crystals, mp 80—81°C in a 63% yield, which was identified as *o*-aminodiphenylamine by a mixed-melting-point test with an authentic sample and by a study of its infrared spectrum.

Reaction between 1, 2-Diimino-3, 5-cyclohexadiene and Cyclopentadienyl Cobalt Dicarbonyl. An ether solution of 1, 2-diimino-3, 5-cyclohexadiene was prepared by the oxidation of *o*-phenylenediamine according to the method of Willstätter and Pfannensteil.[5] To this orange-red solution, cyclopentadienyl cobalt dicarbonyl was added and the mixture was stirred for 6 hr at 0°C. The solution was evaporated, and the residue was treated to yield the complex IIIc in a 0.3% yield, mp 179—180°C.

Found: C, 57.49; H, 4.74; N, 12.34%. Calcd for $C_{11}H_{11}N_2Co$: C, 57.40; H, 4.82; N, 12.17%.

IR: 3320(m), 1570(w), 1540(w), 1465(m), 1405(w), 1371(s), 1340(sh), 1195(m), 1106(m), 1046(w), 889(s), 915(w), 817(s), 743(vs) cm^{-1}.

Reaction between *o*-Aminodiphenylamine and Cyclopentadienyl Cobalt Dicarbonyl. A mixture of 1 g of cyclopentadienyl cobalt dicarbonyl and 1.8 g of *o*-aminodiphenylamine was heated at 150—160°C for 6 hr under nitrogen. The reaction mixture was then extracted with benzene (5 m*l*) and chromatographed on alumina, using a mixture of *n*-hexane and benzene (1 : 1) as a developer. Recrystallization from *n*-hexane gave the crystals of IIIa in a 0.6% yield.

Reaction between *o*-Phenylenediamine and Cyclopentadienyl Cobalt Dicarbonyl. A solution of 3 g of *o*-phenylenediamine and 2.5 g of cyclopentadienyl cobalt dicarbonyl in 50 m*l* of benzene was stirred at room temperature in air for 20 hr. During this period, the color of the solution changed from red-brown to red-purple. From the reaction mixture, the complex IIIc was then isolated in a 6.4% yield by a procedure similar to that described above.

Reaction of IIIc and Carbon Monoxide. The IIIc complex (55 mg) in benzene (20 m*l*) was reacted with 100 kg/cm² of carbon monoxide at 200°C for 4 hr. From the reaction mixture, cyclopentadienyl cobalt dicarbonyl (trace) and benzimidazolone (72% yield) were obtained. The former was identified by a study of its infrared spectrum, while the latter was identified by a mixed-melting-point test with an authentic sample and by a study of its infrared spectrum.

Results and Discussion

Complexes with a different structure from those of the complexes previously reported were obtained by the reaction of aromatic azo compounds with

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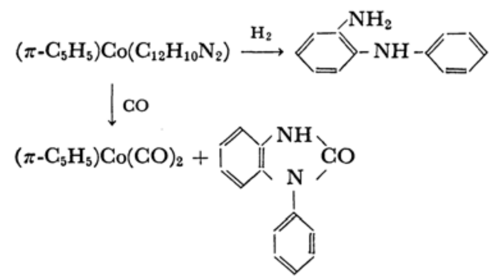
[4] R. L. Clark and A. A. Pessolano, *J. Am. Chem. Soc.*, **80**, 1657 (1958).

[5] R. Willstätter and A. Pfannensteil, *Ber.*, **38**, 2348 (1905).

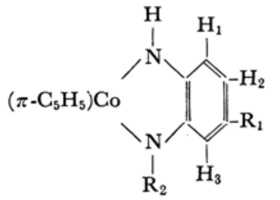
cyclopentadienyl cobalt derivatives. Thus, azobenzene or 4, 4′-dimethylazobenzene reacted with cyclopentadienyl cobalt dicarbonyl or dicyclopentadienyl cobalt at 135—160°C under nitrogen both in the absence and in the presence of a solvent. The reaction products were chromatographed and recrystallized from *n*-hexane to yield red-purple crystals of a cobalt complex, $(\pi\text{-}C_5H_5)Co(C_{12}H_{10}N_2)$ or $(\pi\text{-}C_5H_5)Co(C_{14}H_{14}N_2)$ respectively. These new complexes are stable in air and melt without decomposition. They are soluble in most organic solvents, but are insoluble in water, and they gradually decompose in carbon tetrachloride.

The infrared spectra of these compounds possess a sharp absorption band at 3300 cm^{-1}, attributed to the N–H bond.

The $(\pi\text{-}C_5H_5)Co(C_{12}H_{10}N_2)$ complex obtained from azobenzene reacted with carbon monoxide at 200°C to produce *N*-phenyl-benzimidazolone and cyclopentadienyl cobalt dicarbonyl. By reaction with hydrogen, on the other hand, it gave *o*-aminodiphenylamine.



It may be considered from the above-mentioned experimental evidence that the complexes of cobalt have the IIIa and IIIb structures respectively.



(III)

IIIa: $R_1=H$, $R_2=C_6H_5$
IIIb: $R_1=CH_3$, $R=p\text{-}C_6H_4\cdot CH_3$
IIIc: $R_1=R_2=H$

Further support for the proposed structure (III) for the complexes is given by the fact that the complex IIIc was obtained as stable red-purple crystals from the reaction of 1, 2-diimino-3, 5-cyclohexadiene[5)] with cyclopentadienyl cobalt dicarbonyl in an ether solution. The complex IIIc is the parent compound in a series of the complexes III and reacts with carbon monoxide to give benzimidazolone.

Either the IIIa or IIIc complex was also obtained when *o*-aminodiphenylamine or *o*-phenylenediamine was treated with cyclopentadienyl cobalt dicarbonyl.

The nuclear magnetic resonance spectra of these complexes can be explained on the basis of the structures, IIIa, IIIb and IIIc. The results are summarized in Table 1. No signals attributable to the NH protons appeared, probably because of the spectra's broadness.

The accumulated experimental evidence is thus in agreement with the proposed structure of the isolated cobalt complexes.

It is rather surprising that the coordination of azobenzene to cobalt is accompanied by the migration of the phenyl group of azobenzene and has resulted in the formation of the diamide of *o*-aminodiphenylamine. Bagga and his co-workers[3)] proposed the structure II for their azobenzene complex of iron, in spite of the formation of *o*-semidine on the reduction of their complex with lithium

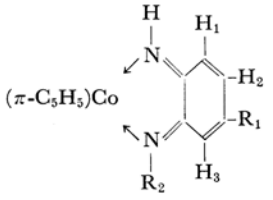
TABLE 1. NMR SPECTRA OF THE COMPLEX

Compound	Line position (τ)	No. of protons	Structure	Assigment
IIIa	5.36	5	Singlet	Cyclopentadienyl ring
	3.08	4	Complex	H_1, H_2, H_3 and $R_1=H$
	2.55	3	Complex	Phenyl ring (R_2)
	2.26	2	Complex	
IIIb	8.32	3	Singlet	Methyl group
	7.55	3	Singlet	Methyl group
	5.46	5	Singlet	Cyclopentadienyl ring
	3.70	1	Singlet	H_3
	3.38	1	Doublet*	H_1 and H_2
	3.28	1	Doublet*	
	2.79	2	Doublet**	Phenyl ring (R_2)
	2.52	2	Doublet**	
IIIc	5.17	5	Singlet	Cyclopentadienyl ring
	3.25	4	Complex	H_1, H_2, H_3 and $R_1=H$

(* $J=5$ cps ** $J=5$ cps)

aluminum hydride. However, no detailed experimental results have been reported in the literature.

The structure IV, an alternative to the structure III, can also be considered for the cobalt complexes mentioned above. At present, it is uncertain which is the more favorable of the two structures, III or IV.



(IV)

The metal complexes reported in the literature to contain *o*-quinonediimine as ligands are those of $M[C_6H_4(NH)_2]_2$ (M=Ni, Pd, Pt and Co).[6,7] Moreover, complexes containing a similar ligand structure, such as $Fe_2(CO)_6C_6H_4SNH$ and $Fe_2(CO)_6C_6H_4S_2$, have been reported in the literature.[8]

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[6] A. L. Balch, F. Röhrscheid and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

[7] E. I. Stiefel, J. H. Waters, E. Billig and H. B. Gray, *ibid.*, **87**, 3016 (1965).

[8] T. A. Manuel and T. J. Meyer, *Inorg. Chem.*, **3**, 1049 (1964).